

AD-A154 642 UNDERSTANDING AND LABORATORY PREDICTION OF THE  
ATMOSPHERIC CORROSION BEHA. (U) CENTRE BELGE D'ETUDE DE  
LA CORROSION BRUSSELS M POURBAIX 31 JAN 84  
UNCLASSIFIED DAJA45-83-C-0011 F/G 11/6

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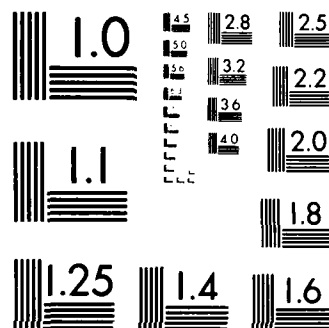
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UNDERSTANDING AND LABORATORY PREDICTION OF THE ATMOSPHERIC CORROSION  
BEHAVIOR OF STEELS AND OF NON-FERROUS METALS AND ALLOYS.

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## SUMMARY OF THE FIRST SEMI-ANNUAL REPORT

Analysis of the literature indicates that a linear bilogarithmic law  $\log p = A + B \log t$  is valid for weight losses of several aluminum alloys in several atmospheres. However, weight loss may not be a suitable way to report results of all exposure tests, because localized corrosion (pitting, intergranular, exfoliation, cracking) may affect the engineering use of aluminum alloys. Local corrosion penetration depth and loss in tensile strength may be of greater engineering significance, in some cases.

An accelerated electrochemical test method for atmospheric corrosion was developed by CEBELCOR for bare steels. In the present programme, this accelerated method was used for the first time to evaluate non ferrous metals or coatings: galvanized steel, steel coated with 55%Al-Zn (Galvalume or Aluzinc), aluminum-manganese, aluminum-copper-magnesium and aluminum-copper-magnesium-zinc alloys. The method gave significant results: for galvanized steel, Al-Zn coated steel and aluminum, higher values of electrode potentials measured during the accelerated test indicate a greater tendency to passivation. Preliminary results of the accelerated test seem to agree well with results of natural exposure tests. Also, the electrode potentials measured during the accelerated electrochemical test proved to be meaningful.

## 1. LITERATURE SURVEY

The major contribution from the literature on the atmospheric corrosion of aluminum alloys includes a large series of results of an ASTM test campaign, under Committee B-3 (1,2), discussions on specific characters such as crevice corrosion and galvanic corrosion (2,3) and discussions on the significance of results of atmospheric corrosion tests of aluminum alloys for ranking alloys, evaluation of corrosivity of environments, decrease of corrosion rate with time and for life prediction.

Aluminum alloys may suffer general corrosion in severe industrial atmospheres, but in most cases, corrosion of aluminum and aluminum alloys is localized: pitting, or intergranular corrosion (for example on Al-Cu alloys 2024-73, T36, T81, T86 in marine and industrial environments, and on Al-Cu-Mg-Zn alloys 7075-T6 in all kinds of environments), or exfoliation or lamellar splitting (for example on 2024-T36 and 7079-T6 in marine conditions).

For this reason, results are not only expressed as weight loss versus time but also as maximum corrosion penetration depth and as loss in tensile strength versus time.

Two papers discuss the initial period of exposure: CARTER and CAMPBELL (4) emphasize that initial exposure in winter time may result in corrosion penetration depth 1.5 to 2.5 times greater than for initial exposure during summer time. SOWINSKI and SPROWLS (3), quoting BARTON (5), illustrate three stages in the atmospheric corrosion of aluminum: during the induction period, a sub-microscopically thick oxide film is formed and then breaks down locally, with initiation of local metal dissolution. During a transition period, which may last for up to 5 years or more, corrosion products precipitate on local sites of attack, and corrosion rate decreases. During the final period, new local sites of attack are formed, with either a constant or a slowly decreasing corrosion rate.

SOWINSKI and SPROWLS (3) give an important index of a large number of papers giving results of a large number of test campaigns all over the world.

One of the largest programme was initiated in 1958 by ASTM Committee B-3 and was due to last for 20 years. The results after 1, 2 (1) and 7 (2) years have now been published. The programme includes 38 aluminum alloys (clad or bare) in 9 sites, including tests performed in Great-Britain and reported by CARTER (6).

An extension of this programme was carried out simultaneously by Reynolds Metals at four other sites, and is reported by ALLOR (7).

From these results, we have considered those relating to alloys which may be compared to the three aluminum alloys which are included in our experimental programme (Table 1): field results for pure Al, 5083 and Al 7075-T6.

were used for comparison with accelerated testing of Al-Mn alloy 3103-H24; field results are available for the Al-Cu alloy 2024-T81. No field results were found for the Al-Mg-Cu-Zn alloy 7075-T73. Field results are available for this composition, but for the temper T6 which is known to produce lamellar splitting under all types of atmospheric exposure conditions.

Field results for these alloys are reported in table 2 after 1 year (when available, after 2 and after 7 years. Results are expressed as weight loss per unit of area after given days of exposure, as average depth of the 4 deepest pits, as loss in ultimate strength (%) and loss in elongation (%).

The codes and characteristics of the test sites are given in table 3. General descriptions such as distance from the sea or from industries are far from enough to allow valid comparisons between different or similar test sites. Average time of wetness (or time with a relative humidity higher than 85%), surface temperature of the samples during wetness, airborne chloride pollution and airborne SO<sub>2</sub> pollution are considered as the main parameters necessary to fully characterize an atmospheric corrosion test station. Such data are available only for two test sites at Kure Beach, and for the last two years of the seven years test period (8). Time of wetness is measured by an electrical device where a potential difference appears between a corroding metal and platinum wires placed very close, on a flat panel. Chloride pollution is measured by the wet candle method, and SO<sub>2</sub> pollution is measured by the lead peroxide method. It is suggested to add pH of rain water to the parameters necessary to characterize a corrosion testing station.

The following comments can be made, on the results of these natural exposure corrosion tests:

- the absolute amount of corrosion is much dependent on the local conditions at the test site, and this is especially true for industrial sites. Figure 1 illustrates this for pure aluminum, figure 2 for Al-Cu and it can be seen from table 2 for other alloys: corrosion is much more severe at Sheffield and even in a residential district of London (Euston) than at other industrial sites such as Newark, New-Jersey. By far, the most important corrosion is observed in severe industrial atmospheres such as Sheffield, or Mc Cook.
- corrosion data are scattered for different samples of the same metal at the same location. It is not uncommon to observe larger weight losses after shorter exposure times (see table 2, alloy 2024-T81 at Kure Beach 240m, Mc Cook and Richmond), or larger pit depth after shorter times (see table 2, alloy 3003-H14 at State College, aluminum SI-H at Hayling Island, alloy 7075-T6 at Point Reyes).
- it is rather common to observe pit depths after 1 or 2 years which do not become significantly more important after 7 years, even when weight loss increases significantly (see table 2, aluminum SI-H at Rambury and Amfleson, alloy 3003-H14 in Kure Beach 24m, alloy 2024-T81 at Newark and Point Reyes).

These data suggest that the results of natural exposure tests can be used in the

early periods, with considerable depths in some cases, and that the number of sites for localized attack increases more with time than the depth of the localized attack.

The type of corrosion must be reported together with weight loss, pit depth, loss in strength, loss in elongation and presence of intergranular attack or exfoliation. It is suggested to add an evaluation of the surface percentage which is affected by localized corrosion.

Several attempts were made to describe mathematical relationships between corrosion and time of exposure. M. POURBAIX (9) surveyed a wealth of data on atmospheric corrosion and reported weight losses measured by Inland Steel on aluminized steel in a marine atmosphere and in an industrial atmosphere which obey a linear bilogarithmic relationship  $\log \Delta p = A + B \log t$ .

A similar relationship was found valid also for weight losses reported by CARTER (6) in marine and industrial atmospheres, for pure aluminum, Al-Mg, Al-Mg-Si and clad Al-Cu alloys (10).

SOWINSKI and SPROWLS (3) analyzed results from many test campaigns. Although they report linear relationships between loss of weight and time of exposure (figure 3), between maximum pit depth and log of weight loss (figure 4), or log of maximum pit depth and log of weight loss (figure 5), or log of loss in tensile strength and log of exposure time (figure 6), they finally conclude that the latter is the most probable relationship, and that a linear bilogarithmic law exists between the corrosion damage  $D$  and time of exposure  $D = A t^B$ , or  $\log D = \log A + B \log t$ . It is clearly stated in this paper that the corrosion damage  $D$  may be defined by loss in tensile strength or by maximum pit depth. Apparently (9,10),  $D$  may also be defined as loss of weight.

The authors suggest that the ranking of aluminum alloys may best be obtained by the numerical values of  $A$ . This may be true if  $B$  shows similar values for the alloys considered. We consider that care should be paid not to oversimplify the problem of alloy evaluation for aluminum alloys: as it will be discussed later in this report, the corrosion resistance of aluminum alloys is determined by different mechanisms in different exposure conditions: in severe industrial conditions (low pH), oxide films may be significantly soluble. In moderate industrial conditions, protection by an oxide film may be effective if chloride is not present. In marine atmosphere, local destruction of the film may occur because of chloride. It is thus necessary to clearly characterize the type of atmosphere in which tests are conducted, and not to mix results obtained under conditions where different mechanisms of corrosion are acting.

One of the interest of the experimental part of this programme is to allow tests to be performed in well controlled and constant exposure conditions, which can be selected at will to reproduce all kinds of natural exposure conditions.



These test conditions are realized in an accelerated test, according to an original electrochemical test method. As far as we know, electrode potentials measurements were, till now, never used as a method for studying the atmospheric corrosion of aluminum alloys.

## 2. EXPERIMENTAL

### 2.1 Materials

The aluminum alloys used in the experimental programme are listed in table 1. Three bare alloys (3103-H24, 2024-T81, 7075-T73) and one clad alloy (7075-T73 clad with 7072) were used. No anodized nor chromated samples were considered during this period.

### 2.2 Accelerated test method

The method was described in the first semi-annual progress report (10). One unit of the experimental device is represented in figure 7. The major characteristics of the test conditions are recalled:

Cycle: adjustable. Here: approximately one hour (exactly 53 min)  
           immersion: 13 min  
           emersion: 40 min

Solutions: in this part of the study:

-NaHSO<sub>3</sub> 10<sup>-4</sup> M, to simulate industrial conditions  
           (pH 4.1 to 4.5 during the course of one test)

-artificial sea water (according to ASTM standards D1141-52-1965, without heavy metals), diluted one hundred times, to simulate marine conditions (pH 6.1 to 6.6 for the duration of the test).

The composition of the the test solutions may be adjusted at will to simulate more or less aggressive conditions or combinations of several aggressive pollutants.

Aeration: by bubbling air in the solution, in the test unit.

Flow of solution: the solution is renewed at a flow rate of 3.3 l/day in each test unit.

Number and size of specimens: 6 samples of the same alloy in each test unit.

Typical size is 100mmx20mmx2 or 3 mm.

Drying temperature: adjustable. Here: 60°C on the sample surface.

Six units are working simulatneously; 2 spare units are available for complementary tests.

Electrode potentials were measured twice a day. Typical duration of a test in this study was around 60 days.

Unless otherwise stated, the samples were etched 30 sec in 10% NaOH at 70°C, rinsed, immersed 5 sec in concentrated (70%) HNO<sub>3</sub> at room temperature, rinsed and dried, before the test. Each sample was weighted and then fixed on a stainless supporting rod, the rod and the assembling being cleaned after the test period, the solution was efficiently cleaned and laboratory and the corrosion product

were removed according to ASTM G1-72: 10 min in 2% chromic acid  $\text{CrO}_3$  + 5% phosphoric acid  $\text{H}_3\text{PO}_4$  at 80-85°C, rinse, 1 min in 70% nitric acid  $\text{HNO}_3$  at room temperature, rinse, dry. The operation was repeated three times and the final weight was considered only if it changed less than 0.3 mg between the last two operations.

Pit depth (average of around 30 to 40 deep pits and average of 5 deepest pits) was measured by focusing a microscope.

Typical samples were prepared for metallographic examination: etchant for 3103 was 50 ml Poulton reagent (12 parts concentrated  $\text{HCl}$  + 6 parts concentrated  $\text{HNO}_3$  + 1 part 48%  $\text{HF}$  + 1 part  $\text{H}_2\text{O}$ ) + 25 ml concentrated  $\text{HNO}_3$  + 40 ml of a solution 3 mg  $\text{CrO}_3$  in 10 ml  $\text{H}_2\text{O}$ ,

etchant for 2024 and 7075 was: Keller reagent (2 ml 48%  $\text{HF}$  + 3 ml concentrated  $\text{HCl}$  + 5 ml concentrated  $\text{HNO}_3$  + 190 ml  $\text{H}_2\text{O}$ ).

### 2.3 Outdoor exposure tests

One outdoor exposure test was initiated, for additional informations. One sample of each 3103-H24, 2024-T81 and 7075-T73 was exposed at an angle of 45°, facing south, in a residential area in Brussels, 100 m from a chimney used for oil-heating of a large community (university). A lead peroxide candle was placed just next to the samples, for simultaneous measurements of  $\text{SO}_2$  pollution. A special capillary bridge was developed, with a fine and acute tip, to measure electrode potentials of the samples during rainy periods. The measuring technique is somewhat delicate, because the tip of the siphon of the reference electrode should just touch the water film but not the sample itself. These measurements are intended to help correlating accelerated tests with real local exposure conditions.

### 3. RESULTS

#### 3.1 Accelerated test for atmospheric corrosion

Preliminary tests on 3103-H24, 2024-T81 and 7075-T73 in rural ( $H_2O$ ), industrial ( $NaHSO_3$   $10^{-4}M$ ) and marine (1% sea water) were reported in the first semi-annual progress report, together with preliminary tests on galvanized steel and galvalume (aluzinc)-coated steel.

During the second semi-annual period, fully elaborated tests were conducted on the three aluminum alloys, bare, and on 7075-T73 clad with 7072 (Al-Zn). Electrode potentials, weight losses, pit depths were measured and types of corrosion were identified.

Electrode potentials (at the end of immersion periods) versus time are reported on figures 8 to 14.

It may be observed that the electrode potential of 3103-H24 in  $NaHSO_3$   $10^{-4}M$  is below the  $H^+/H_2$  equilibrium potential, indicated by the letter A on the potential axis (figure 8). In dilute sea water, the electrode potential of 3103-H24 is slightly under or equal to this potential "A" (figure 10).

Alloys 2024-T81 and 7075-T73 show potentials significantly higher (more positive) than the potential "A" in  $NaHSO_3$   $10^{-4}M$ , especially in the case of alloy 2024 which contains more copper and no zinc (figure 9). In diluted sea water, potentials of both these alloys are very similar and just slightly higher than the  $H^+/H_2$  equilibrium potential "A" (figure 11). Cladding 7075 with 7072 results in lower potentials (significantly lower than the "A" values), in both solutions (figures 13 and 14).

Weight losses versus time are shown on figures 15 to 18, and pit depths are represented on figures 19 and 20. When one sample showed few pits, only the average of 4 or 5 deepest pits is plotted.

It is apparent that, in several material-environment combinations, pits of significant depths were formed as early as on the second day of test, and that no significant increase of the maximum pit depth occurred during the rest of the 60 days test period (see for example figure 19, for 2024-T81 and 7075-T73 in  $NaHSO_3$   $10^{-4}M$ ). Some scattering was observed for pit depths (figure 20, 7075-T73) and also for the low values of weight loss. However, weight loss and pit depth curves may give some idea of the corrosion pattern, when considered together: for example, figures 15 and 19 suggest that 3103-H24 suffered general corrosion in  $NaHSO_3$   $10^{-4}M$ , and figures 16 and 20 suggest that 7075-T73 suffered pitting corrosion, apparently with few but deep pits.

Micrographs through typical corroded zones show indeed that 3103-H24 shows no pitting in  $\text{NaHSO}_3$   $10^{-4}\text{M}$ , but that a few areas show many shallow pits in dilute sea water.

2024-T81 and 7075-T73 show average size pits in  $\text{NaHSO}_3$   $10^{-4}\text{M}$ ; in dilute sea water, 7075-T73 has a few very deep pits and 2024-T81 suffers serious intergranular corrosion, also indicated by a considerable loss of weight and by a large corrosion penetration.

In these accelerated tests,  $\text{NaHSO}_3$   $10^{-4}\text{M}$  was selected to simulate industrial environments. This test solution has a pH between 4.1 and 4.5. Rain water with pH as low as 3.7 have been reported and it is likely that our test solution should be more concentrated to simulate more severe industrial environments. Artificial sea water diluted one hundred times was selected to simulate marine environments. In this case also, the sea water dilution should be adjusted to simulate more closely a given marine condition. Local pollution and climatic measurements and in situ measurements of electrode potentials are expected to help to better adjust the simulated conditions for this accelerated test.

### 3.2 Outdoor exposure tests

The experimental arrangements described under section 2.3 will provide informations in a next research period.

Preliminary measurements were made on different metallic structures in a residential area, which were aimed at defining the best measuring procedure. Measurements should be made when the metallic surfaces are naturally wet (because of rain or dew); the tip of the capillary siphon should touch the liquid film but not the solid surface of the metal; reliable measurements were obtained when using a  $10^{-3}\text{M}$   $\text{Na}_2\text{SO}_4$  solution in the capillary bridge.

The preliminary measurements of "in situ" electrode potentials during rain are:

on aluminum (exposed for 4 years):

- 480 to - 525  $\text{mV}_{\text{Sce}}$ ,

(and -1000 to -1100  $\text{mV}_{\text{Sce}}$  on a freshly scratched surface)

on galvanized steel (exposed for 4 years):

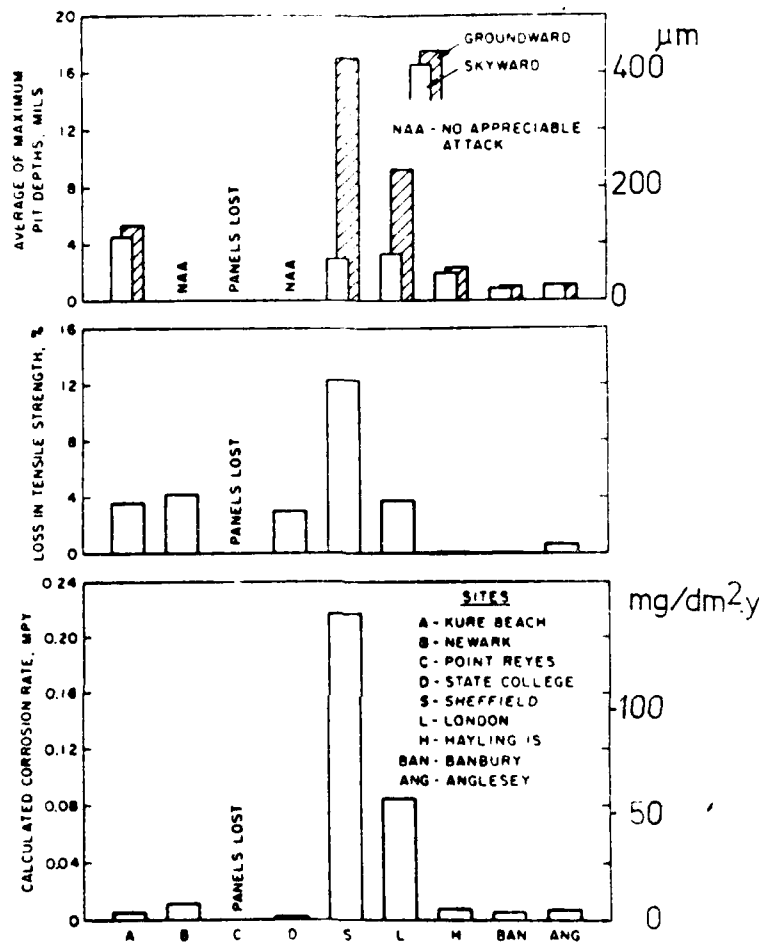
-950 to -980  $\text{mV}_{\text{Sce}}$ ,

(and -1050  $\text{mV}_{\text{Sce}}$  on a freshly scratched surface)

on weathering steel (exposed for 6 years):

-250  $\text{mV}_{\text{Sce}}$ ,

(decreasing to -320  $\text{mV}_{\text{Sce}}$  on a scratch which did not reach the bare metal).



**Figure 1** Comparison of corrosion effects at different test sites for pure aluminum (1199-H18 and S1-II), after 7 years (from (2), p 151)

TABLE 3

Codes and description of the test sites considered in table 2

Rural sites

St.C: State College, Pa. Located one mile N of State College, Pa.  
No industrial contamination.  
Samples face SE.

BAN: Banbury, England Located 2 miles N of Banbury. Atmospheric  $\text{SO}_2$  is about 1/10 of that observed in London. Samples face prevailing winds, SW.

Industrial sites

NWK: Newark, N.J. Moderately severe industrial. The area is surrounded by chemical plants and oil refineries. Samples face SSW.

EST: Euston (London), England Moderately severe industrial. Residential and light industrial section of Euston, on top of BNFMA Laboratories. Fumes from heating systems of buildings, BNFMA laboratories, railroad station. Samples face prevailing winds, SW.

RCH: Richmond, Va. Moderate industrial. 10 miles south of Richmond, Va., on Reynolds Metals extrusion plant. Samples face S.

McC: Mc Cook, Ill. Industrial. In the Reynolds Metals Mc Cook plant. Samples face S.

SHF: Sheffield, England Severe industrial. Located 1 mile NE of center of city, in heavy industrial area, surrounded by industrial chimneys within 65 m. Samples face prevailing winds, SW.

Marine sites

KB240: Kure Beach, N.C. Rural, marine. Located 17 miles SE of Wilmington, N.C., approximately 240 m from the ocean. Samples face S.  
From Dec. 63 to Dec. 65 (8): average monthly time of wetness from 8.7 to 21.5 days, with an average 16.3 days, i.e. 53.5 % of time.  
surface temperature of samples during wet periods: monthly average from 6.7°C to 25.8°C, average 15.3°C.  
airborne chloride: monthly average from 4.0 to 41.0 mg  $\text{Cl}^-/\text{m}^2\cdot\text{day}$ , average 16.43 mg  $\text{Cl}^-/\text{m}^2\cdot\text{day}$ .  
airborne  $\text{SO}_2$ : monthly average from 0.032 to 0.176 mg  $\text{SO}_2/\text{dm}^2\cdot\text{day}$ , average 0.0912 mg  $\text{SO}_2/\text{dm}^2\cdot\text{day}$ .

KB24: Kure Beach, N.C. East coast marine. Located on Cape Fear Peninsula, 24 m from the ocean. Samples face ESE, parallel to the beach. From Dec. 63 to Dec. 65 (8):  
time of wetness: monthly average from 11.7 to 29.5 days, average 22.5 days, i.e. 74.1 % of time.  
surface temperature of samples during wet periods: monthly average from 5.9 to 24.6°C, average 15.2°C.  
airborne chloride: monthly average from 14.2 to 343.0 mg  $\text{Cl}^-/\text{m}^2\cdot\text{day}$ , average 125.4 mg  $\text{Cl}^-/\text{m}^2\cdot\text{day}$ .  
airborne  $\text{SO}_2$ : same as Kure Beach 240 m.

Pt.R: Point Reyes, Ca. West coast marine. Located 65 m from ocean behind low hills. Samples face W. Salt spray and condensation from westerly winds. Samples are wet most of the winter, and dry in summer days but wet most of the night.

WAT: Wavling Island, England Located at the head of an inlet, 100 m from the sea and 1.1 km above normal high water level. Water runs under the island when each tide. No industrial contamination.

WGL: Wexley, England Located 1 km from high water mark on Wexley. Salt spray condensation in winter. No industrial contamination.

WIL: Wilkes-Barre, Pennsylvania Located 10 miles from Corpus Christi, on the Gulf of Mexico. Samples face S. Approximately 1 km from the North Texas coast.



TABLE 2

Results from field tests from ASTM B-3 programme (2) and from a programme of Reynolds Metals (7)

Alloy	days	site	weight	pit depth			loss in	loss in
ASTM nr	exposed		loss	(avg 4 deepest)			strength	elongation
d: density			mg/dm <sup>2</sup>	µm			%	%
				sky	ground	avg <sup>(1)</sup>		
SI-H (2 and 7 years nr 87 d = 2.70)	730	KB24 m	9.5	90	100	95	2	0
	734	NWK i	15.2	-	2	2	2	0
	501	Pt.R m	4.8	40	52	47	0	0
	735	St.C r	3.9	-	-	-	1	0
	719	SHF i	309.2	12	175	130	6	44
	735	EST i	139.8	70	192	132	3	37
	726	HAY m	12.8	62	62	62	1	5
	735	BAN r	10.4	45	15	30	3	0
	780	ANG m	12.0	40	37	40	1	2
	2557	KB24 m	25.17	112	132	122	3.6	0
	2558	NWK i	52.47	-	-	-	4.2	0
	2333	Pt.R m	-	-	-	-	-	-
	2538	St.C r	10.89	-	-	-	3.0	0
	2207	SHF i	999.6	72	425	250	12.3	16.7
	2191	EST i	348.8	82	230	157	3.7	0
	2184	HAY m	32.53	47	57	52	0	0
	2191	BAN r	23.57	37	30	35	0	0
	2171	ANG m	28.34	40	40	40	0.6	0
3003-H14 (2 and 7 years) nr 22 d = 2.73	730	KB24 m	16.88	42	37	40	0	7
	734	NWK i	31.35	30	45	37	1	7
	744	Pt.R m	12.50	25	45	37	0	7
	735	St.C r	4.44	52	40	47	0	7
	2557	KB24 m	55.92	42	35	40	0.9	5.1
	2558	NWK i	120.2	35	77	62	1.4	0
	2568	Pt.R m	26.68	15	40	27	0	0
2538	St.C r	13.56	2	2	2	0	0	
2024-T81 (1, 2 & 7 years) nr 32 d = 2.77	362	KB24 m	35.40	35	25	30	1	20
	391	CC m	61.78	52	50	52	0	25
	364	RCH i	103.6	35	52	45	2	34
	364	McC i	332.9	77	100	90	8	32
	730	KB24 m	52.2	57b	90b	72b	3	20
	734	NWK i	72.4	52b	65b	60b	1	13
	744	Pt.R m	51.5	80b	100b	90b	3	32
	735	St.C r	10.9	75	50	30	2	0
	734	KB240m	19.38	27	32	30	1	17
	744	CC m	51.56	30b	55b	42b	1	32
	725	RCH i	164.6	62b	62b	62b	7	27
	731	McC i	225.0	80b	65b	72b	10	37
	2557	KB24 m	108.0	82	80	82	6.5	32.7
	2558	NWK i	173.4	57	77	67	5.6	21.8
	2576	Pt.R m	99.34	62	90	77	7.3	49.1
	2538	St.C r	23.37	15	52	35	2.1	3.5
	2525	KB240m	63.63	82	70	75	2	35
	2560	CC m	55.30	82b	77b	80b	3	28
	2511	RCH i	117.0	102b	110b	107b	7	38
	2545	McC i	434.2	187b	142b	165b	14	51
2025-T6 (2 and 7 years) nr 24 d = 2.70	730	KB24 m	50.015	87b	62b	72b	3	6
	734	NWK i	31.848	70b	67b	70b	7	6
	744	Pt.R m	47.156	72b	140b	107b	1	28
	735	St.C r	61.582	71	-	75	0	0
	2557	KB24 m	45.1	70b	65b	70b	1	15.4
	2558	NWK i	124.6	62b	62b	62b	1	24.4
	2568	Pt.R m	104.6	70b	75b	75b	1	26.4
	2538	St.C r	16.6	71	71	71	1	0

m: metric; b: non-metric; i: interior; r: roof; sky: sky; g: ground; avg: average of test specimens

(1) type of site: converted from the test specimen

d: interior; m: metric

TABLE 1

Aluminum alloys included in the experimental programme and aluminum alloys tested in natural conditions considered for comparison

ALLOY	n°	COMPOSITION, WEIGHT PERCENT									
		Al	Cu	Fe	Si	Mn	Mg	Zn	Cr	Ti	Ni
<u>Aluminum alloys included in this experimental programme</u>											
3103-H 4 (1)		bal	0.10α	0.70α	0.50α	0.9-1.5	0.10α	0.20α	0.10α	0.10α	-
2024-T81 (2)		bal	3.8-4.9	0.50α	0.50α	0.3-0.9	1.2-1.8	0.25α	0.10α	-	-
7075-T73 (3)		bal	1.2-2.0	0.50α	0.40α	0.30α	2.1-2.9	5.1-6.1	0.18-0.28	0.20α	-
7075-T73 clad cladding: 7072		bal	0.10α	Fe + Si = 0.70α		0.10α	0.10α	0.8-1.3	-	-	-
<u>Aluminum alloys considered for comparison</u>											
51-H	87	bal	0.0015	0.0035	0.0025	0.0005	-	-	-	-	-
3003-H14 (4)	22	bal	0.13	0.59	0.24	1.01	0.01	0.07	0.00	0.01	-
2024-T81 (2)	32	bal	4.49	0.35	0.20	0.55	1.44	-	-	-	-
7075-T6 (5)	28	bal	1.75	0.25	0.13	0.09	2.60	5.81	0.20	0.03	-

α maximum

(1) H4 is a BS designation. AFNOR and ASTM designation is H24: strain hardened, annealed half hard.

(2) T81: solution treatment 493°C, water quench at room temperature, cold stretching 1.5 to 3.0 %, aged 12 hrs at 190°C

(3) T73: solution treatment 482°C, water quench at room temperature, aged 6 to 8 hrs at 107°C then 24 to 30 hrs at 163°C or (if heated at 14°C/h) 14 to 18 hrs at 168°C.

(4) H14: strain hardened, half hard

(5) T6 : solution heat treatment 482°C, water quench at room temperature, aged 24 hrs at 121°C or 4 hrs at 96°C + 8 hrs at 157°C.

- Figure 16: Weight loss versus time for 3103-H24, 2024-T81 and 7075-T73 (bare, etched) in 1 % sea water.
- Figure 17: Weight loss versus time for 3103-H24 (bare, as received) in 1 % sea water.
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- Figure 15: Weight loss versus time for 3103-H24, 2024-T81 and 7075-T73 (bare, etched) in  $\text{NaHSO}_3$   $10^{-4}$  M.

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The laboratory method proved to be useful to quickly identify the corrosion mechanisms (active dissolution, film formation, pitting corrosion). Additional work should be done to evidence the role of Cu in 2024-T81, in industrial conditions (film formation, or galvanic effect due to redeposited Cu). A film formation mechanism could be identified for 7075-T73 in industrial atmosphere.

Plans for future work, during the second year of the programme, include:

- extensive laboratory tests using the accelerated method with various experimental conditions:
  - more acid  $\text{NaHSO}_3$  solutions,
  - longer wet periods,
  - lower drying temperature,
  - more dilute sea water
  - combined  $\text{NaHSO}_3$  and dilute sea water test solutions,
- extensive laboratory tests using the accelerated method on specimens of other aluminum alloys, of which the practical behavior is known (7075-T6, 6061-T4 or 6061-T6, 5154-H34),
- laboratory tests on anodized and chromated aluminum alloys and on aluminum alloys which were previously corroded and which were subsequently rinsed and treated with corrosion inhibitors (fluosilicate and chromate).

All these tests will last for 60 days or more. Fewer intermediate investigations will allow more tests to be conducted simultaneously. Electrode potentials, weight loss, pit depth and type of corrosion will be recorded, as during the present period.

- surface investigations of 2024-T81 after laboratory test in  $\text{NaHSO}_3$   $10^{-4}$  M (search for selective dissolution and copper redeposition),
- electrode potential measurements on aluminum alloys exposed to natural conditions which are characterized by  $\text{SO}_2$  and  $\text{Cl}^-$  pollution measurements,
- initiation of laboratory tests with the accelerated test method on high strength steels.

All these tests will be interpreted in terms of:

- influence of the experimental conditions of accelerated tests (pH, chloride concentration...) on the type of corrosion and on corrosion rates,
- correlation between results of accelerated tests and known behavior in real exposure conditions,
- correlation between corrosion behavior (for example type of corrosion) and the values of electrode potentials,
- attempts of prediction of behavior in real exposure conditions from results of

years, but it is at least necessary to be able to study these processes separately, before studying the effects of changing conditions. Moving structures such as ships and airplanes are exposed to changing conditions which may be simulated in sequences, with this laboratory test.

Comparison between given experimental conditions for the laboratory test and given real exposure conditions were suggested, with care: for example, 100 days of laboratory test in  $\text{NaHSO}_3$   $10^{-4}$  M (drying temperature  $60^\circ\text{C}$  and one hour-cycle) was suggested to reproduce the corrosion penetration observed after 2 years at the industrial site of Newark, but this is certainly not valid for the much more severe atmosphere of Sheffield. In a similar way, 44 days of laboratory test in 1 % sea water (drying temperature  $60^\circ\text{C}$ , one hour-cycle) was suggested to reproduce 2 years at the marine sites of Kure Beach (24 m from the ocean) and Point-Reyes. However, much care is recommended for the use of these figures at this time.

The accelerated laboratory test method is able to produce distinct types of corrosion (general, pitting, intergranular...) which correspond very well with what is observed in practice. The laboratory method is thus suitable to select alloys which do not suffer from these types of corrosion in given environmental conditions, and to screen the environmental conditions which are unacceptable for given alloys.

An important result of this test method is that severe *intergranular* corrosion was quickly identified for the Al-Cu 2024-T81 alloy in marine simulated conditions, but not in a given industrial simulated condition.

The alloy Al-Cu-Mg-Zn 7075-T73 was not found susceptible to intergranular corrosion, neither in marine nor in industrial simulated conditions. This confirms the improvements brought by the T73 temper, compared with bad field results for the T6 temper.

At this time, we feel most necessary to conduct more laboratory tests, with fewer intermediate measurements, but in many more environmental conditions and mainly in more acid solutions, in combined acid- and chloride containing solutions, and during longer wet periods and at lower drying temperatures.

We also feel necessary to conduct tests on other alloys for which results of real exposure tests are available: especially the Al-Cu-Mg-Zn alloy 7075-T6, which is known to suffer intergranular and lamellar corrosion, and also the Al-Mg-Si alloy 6061-T4 or 6061-T6 and the Al-Mg alloy 5154-H34. Even if some of these alloys are not of direct interest for aircrafts, they will help to calibrate the experimental conditions of the laboratory test.

## 5. PROVISIONAL CONCLUSIONS AND PLANS FOR FUTURE WORK

Results of published real exposure atmospheric corrosion tests indicate a large scattering between results at different locations for apparently similar environmental conditions, and a large scattering of localized corrosion penetrations measured at different times of exposure.

The former effect is related to large effects of slight differences in environmental conditions. This is especially important for aluminum alloys in the case of industrial atmospheres. The latter effect is probably related to the corrosion mechanism itself, with limited propagation of localized corrosion, at least for some aluminum alloys.

It is now recognized that some parameters are important to characterize and to compare real exposure testing stations. These are:

- time of wetness (or time with relative humidity higher than 85 %),
- temperature of the specimen surface,
- pH of rain water or dew,
- airborne chloride pollution,
- airborne SO<sub>2</sub> pollution.

No natural exposure tests should be further conducted without recording these parameters. We advocate to add to these the periodic measurement of electrode potential of the specimen during wet periods, according to a procedure which is described in this report.

From the literature, significantly dangerous corrosion is encountered in very severe industrial conditions (and this may be equally dangerous for all aluminum or aluminum alloys) and also in marine conditions for some alloys and tempers, for which intergranular corrosion, lamellar corrosion and stress corrosion may occur.

Many attempts were made to rank alloys or atmospheres for their corrosivity, using mathematical modelisation of corrosion versus time relationships.

Relationships of the type  $D = A t^B$ , or  $\log D = \log A + B \log t$  (where  $D$  = weight loss, or pit depth, or loss in strength) is rather generally applicable, although  $A$  and  $B$  may show very different values depending on the atmosphere and on the type of damage represented by  $D$ . The different types of corrosion and of corrosion mechanisms were apparently underestimated in several published studies of the atmospheric corrosion of aluminum.

One of the interesting aspects of the CEBELCOR's accelerated laboratory test developed and used in this programme is the possibility to adapt the experimental conditions to simulate all kinds of environments. In this way, a given and constant environment can be studied separately. Nature and seasons are naturally changing, and so are the corrosion processes occurring during the seasons and



#### 4.3 Understanding corrosion processes

Several points related to the corrosion processes were discussed already: general dissolution (without pitting) may occur in acid industrial conditions and is detected by simple electrode potential measurements during testing. Laboratory testing may help to identify the border between conditions leading to active dissolution and conditions leading to the formation of an oxide film. Electrode potential measurements during "in situ" testing may provide the same type of informations.

Potential measurements indicate some effects of alloying elements: a more or less protective oxide film is most probably formed on Al-Cu-Mg-Zn 7075-T73 in  $\text{NaHSO}_3$   $10^{-4}$  M solution, while Cu may be redeposited on Cu-rich aluminum alloy 2024-T81. Surface analysis should demonstrate this, and our accelerated test is a convenient method to prepare specimens in well controlled environmental conditions.

Pitting corrosion of aluminum and aluminum alloys in atmospheric conditions has certainly many factors in common with their pitting corrosion when immersed in aqueous solutions. Local conditions in the pits are one of these important common features which may explain the self limiting character of the propagation of pits in some cases, and the regular growth of pits in some other cases. The significant loss in elongation, compared to the loss in tensile strength (see table 2) is another feature which may be related to local conditions in pits where hydrogen may evolve more readily. Detailed studies on local chemical and electrochemical conditions in pits of aluminum alloys of various compositions should help to understand these questions.

in chloride solution do not exhibit systematic and significant pH decrease.

In several alloy-environment combinations, significant and almost final pit depths were observed by us already after only 2 days of accelerated test. This is also observed in natural conditions (see table 2: for example for Al Si-H in Euston, Hayling, Banbury and Anglesey, for Al-Mn 3003-H14 in Kure Beach 24m and Point-Reyes).

We have also observed that corrosion versus time curves from accelerated tests may be expressed by mathematical relationships in two cases, which allow extrapolation to longer times and comparison with real exposure tests: the first case relates to Al-Mn 3103-H24 in  $\text{NaHSO}_3$   $10^{-4}$  M, which shows a constant corrosion rate of  $0.29 \text{ mg/dm}^2$  per day of test in the given test conditions. This constant corrosion rate indicates an active dissolution corrosion process without film or solid corrosion products, as already observed previously. Extrapolation to one year gives  $106 \text{ mg/dm}^2$  (or  $3.8 \text{ } \mu\text{m/year}$ ), compared to  $309 \text{ mg/dm}^2$  and  $139.8 \text{ mg/dm}^2$  for Si-H at Sheffield and Euston respectively after 2 years, to  $15.2 \text{ mg/dm}^2$  for Si-H at Newark after 2 years and to  $31.3 \text{ mg/dm}^2$  for 3003-H14 at Newark after 2 years. Based on these latter data, the selected test conditions may provide an acceleration of approximately 100 days of accelerated test for 2 years of real exposure at Newark. For Euston and especially for Sheffield, the test condition of the accelerated test should be made more severe to provide a useful acceleration. The second case where corrosion may be expressed as a mathematical function of time relates to 2024-T81, for which the log of the weight loss is a linear function of log of time (figure 23):

$$\log \Delta p = 1.01 + 0.43 \log t \quad (\Delta p \text{ in } \text{mg/dm}^2 \text{ and } t \text{ in days})$$

Considering the weight loss reported in table 2 for the same alloy at Kure Beach 24 m and at Point Reyes ( $52.2 \text{ mg/dm}^2$  and  $51.5 \text{ mg/dm}^2$  after 2 years), it suggests an acceleration of 44 days of accelerated test for 2 years of exposure at these two stations.

These figures give a very rough idea of the acceleration provided by the accelerated test method, but much care is advocated not to misuse this concept of acceleration.

Natural exposure tests of Al-Cu 2024-T81 in marine atmospheres produced *intergranular* corrosion (table 2), which was also observed in the accelerated test in 1 % sea water. Intergranular corrosion was also observed on 2024-T81 in industrial natural exposure sites, and this should be further investigated in the accelerated test by using more severe test conditions.

*Exfoliation* and *intergranular* attack is reported for Al-Cu Mg-Zn 7075-T6 in all types of environments and it is a well known type of corrosion for this alloy in the T6 condition. At this time, the accelerated test confirms that the T3 heat treatment suppresses this type of corrosion.

The potentials of the three alloys in 1 % sea water are less differentiated, even if 2024-T81 and 7075-T73 show slightly higher potentials than 3103-H24. On the contrary, clad 7075-T73 has significantly lower potentials than unclad 7075-T73, and indeed, the corrosion penetration is also much lower when clad (figures 14, 18 and 20). As pointed out by GROOVER et al. (11), in a nearly neutral chloride solution such as sea water, the highest the potential, the deepest the pits, and there is a so-called "protection potential" below which pit depth is insignificant. Although the absolute value reported for this "protection potential" by GROOVER et al. seems rather high, we believe this concept is true and may also be used in atmospheric corrosion testing in marine atmospheres.

It is important to observe that definitely different corrosion patterns were observed in these accelerated tests for different alloys in different environmental conditions: general corrosion (for Al-Mn 3103-H24 in  $\text{NaHSO}_3$   $10^{-4}$  M), general pitting corrosion (for Al-Cu 2024-T81 and for Al-Cu-Mg-Zn 7075-T73 in  $\text{NaHSO}_3$   $10^{-4}$  M), few shallow (3103-H24 in 1 % sea water) or deep pits (7075-T73 in 1 % sea water), and severe intergranular corrosion (2024-T81 in 1 % sea water).

Limits of environmental characteristics between one or another type of corrosion could be found, using this accelerated test. And compositions of alloys or heat treatments which lead to one or another type of corrosion could also be rapidly identified, using this test.

#### 4.2 Comparison between accelerated test and natural exposure tests

Comparison with results of natural exposure tests is not immediate, because of two main reasons which will be considered separately in this discussion: on one hand, the results of natural exposure tests themselves are much different even in apparently similar types of environments (example: Newark and Sheffield, table 2, figures 1 and 2), and this is understood if one considers that the acidity and the time of wetness may be more pronounced at Sheffield. Indeed, pH of rain water or dew is a most significant parameter for the atmospheric corrosion of aluminum, and a small difference in pH may result either in rapid general corrosion or in satisfactory passivation. On another hand, some results of natural exposure tests are very much scattered along with time, which is indicated for example by deeper pits in the specimens examined after one or two years, compared to samples examined after 7 years.

We have also observed a similar scattering of the pit depth, during the accelerated test, which must apparently be explained by both a statistical aspect in the initiation of pits and by a self limiting process in the propagation of localized corrosion of aluminum alloys. It is known that corrosion pits of iron, carbon steel, stainless steels, copper or titanium contain acid solutions generated by hydrolysis of metallic ions, but from informations received from NACE (12), pits of aluminum

#### 4. DISCUSSION

In this section, comments are derived from the experimental results on:

- what practical informations can be derived from the accelerated tests,
- how the accelerated tests compare with natural exposure conditions,
- what kind of informations do these accelerated tests provide for understanding corrosion processes.

Because the programme is not completed at this time, these comments should be considered as provisional, but they nevertheless appear already meaningful.

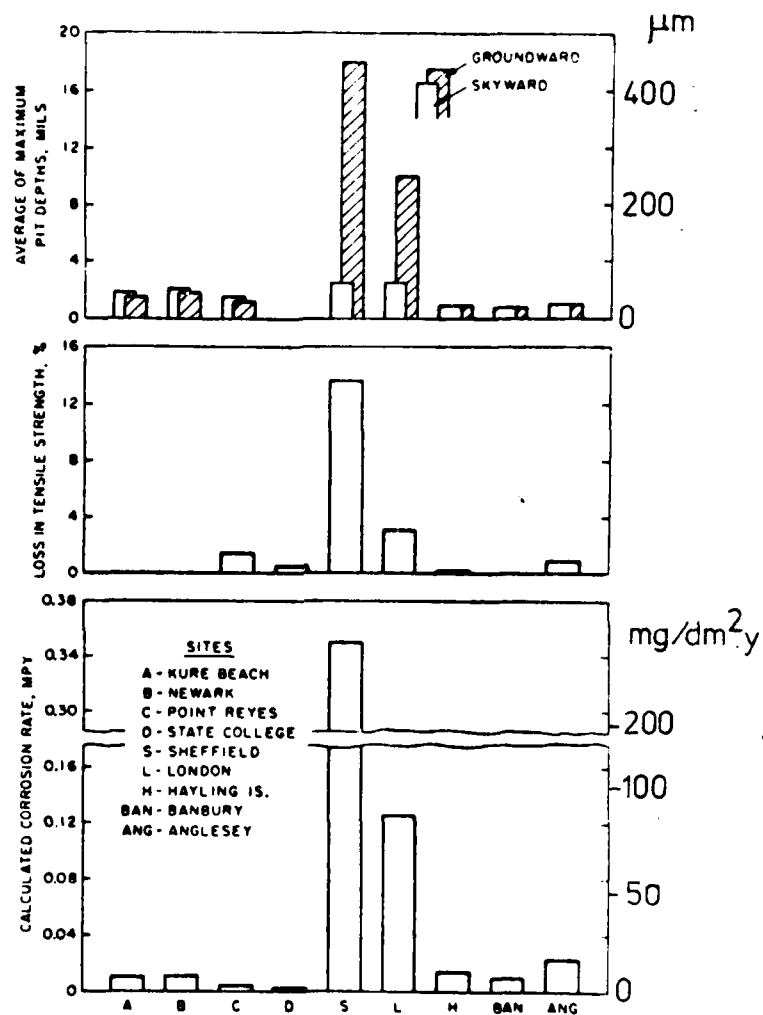
#### 4.1 Practical use of the accelerated test

Basically, the values of the electrode potential indicate the tendency or the absence of a tendency for the formation of an oxide film and, when such a film is formed, they give indications on the quality of the film, which means the presence or absence of more or less severe localized corrosion. They also indicate if evolution of hydrogen is possible.

Rather high potentials (around 0 mV<sub>SCE</sub>) were reported in the first progress report (10) for the three alloys in the "as received" surface condition in distilled water, used as a test solution to simulate rural conditions. It may be expected that even higher potentials (possibly up to +200 mV<sub>SCE</sub>) would be observed on anodized specimens in distilled water.

In  $\text{NaHSO}_3$   $10^{-4}$  M solutions, the potential of 3103-H24 is significantly lower than the  $\text{H}^+/\text{H}_2$  equilibrium potential (represented by "A" in this report) and this means either general corrosion, either the result of a very severe pitting. Since here (figure 8), potentials are below "A" from the very beginning of the test, general corrosion is more likely, and it is confirmed by the significant weight loss (figure 15) and by the rather small local penetration (figure 19) and from the micrograph on figure 21a.

In the same  $\text{NaHSO}_3$   $10^{-4}$  M test solution, alloys 2024-T81 and 7075-T73 exhibit significantly higher electrode potentials (around -200 to -400  $\text{mV}_{\text{sce}}$ ), although not as high as in distilled water. Local penetration (figure 19 and figure 21b,c) indeed suggests the presence of a damaged film, although the copper present in 2024-T81 (3.8 to 4.9 % Cu) could be another reason for the rather high potentials. A closer look at figure 9 shows that the potential of 7075-T73 increases from A (-500  $\text{mV}_{\text{sce}}$ ) at the onset of the test to -300  $\text{mV}_{\text{sce}}$  with subsequent occasional drops of potential: this supports the formation of a film with subsequent pitting. The case of alloy 2024-T81 which exhibits high potentials since the start of the test requires more investigations to see if copper favors for a time the formation of a film, or if copper is readily redeposited.



**Figure 2** Comparison of corrosion effects at different sites for clad Al-Cu alloys (Alclad 2024-T3 and HC15-WP) after 7 years (from (2), p 164).

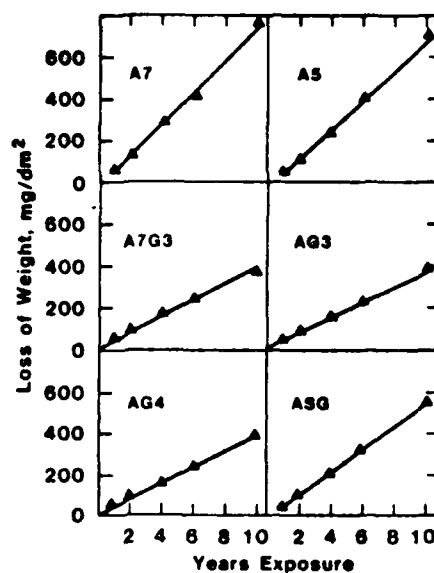


Figure 3 Weight loss of six aluminum alloys versus time of exposure (industrial-marine atmosphere) in Alicante (from (3), p 306).

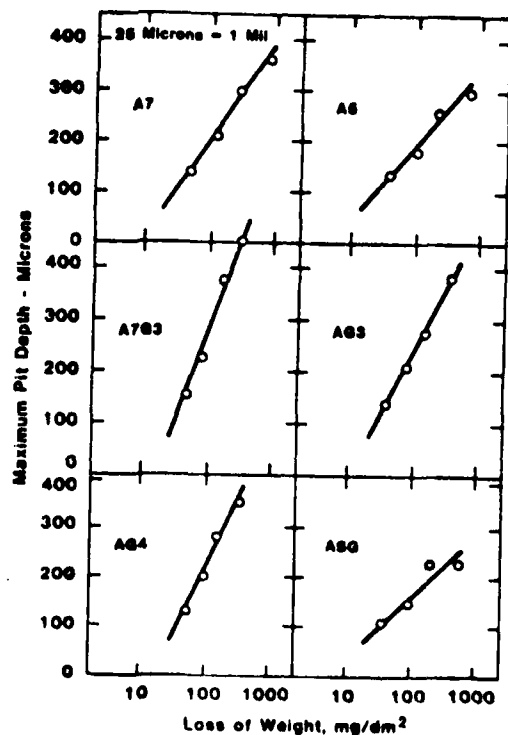
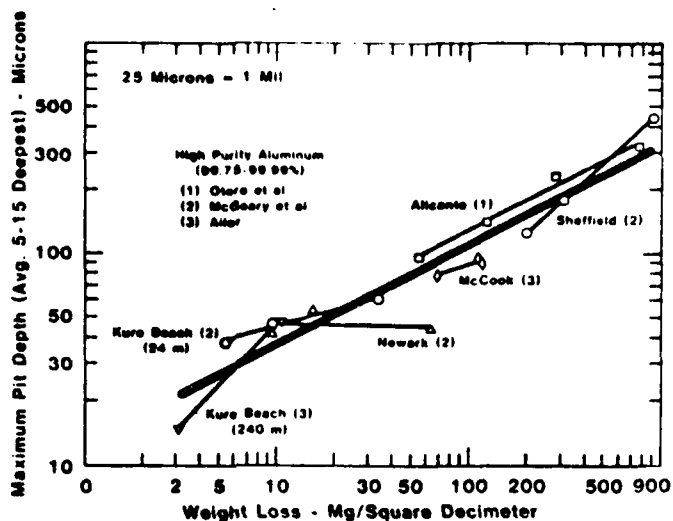
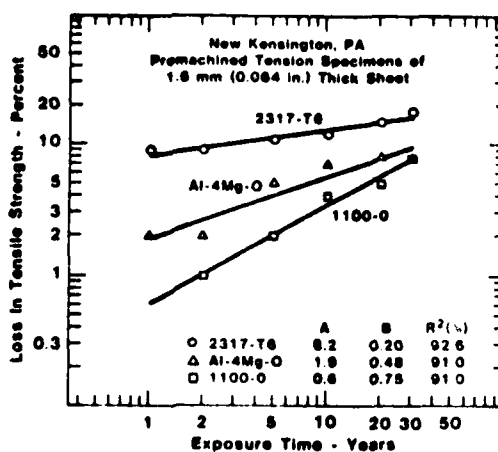


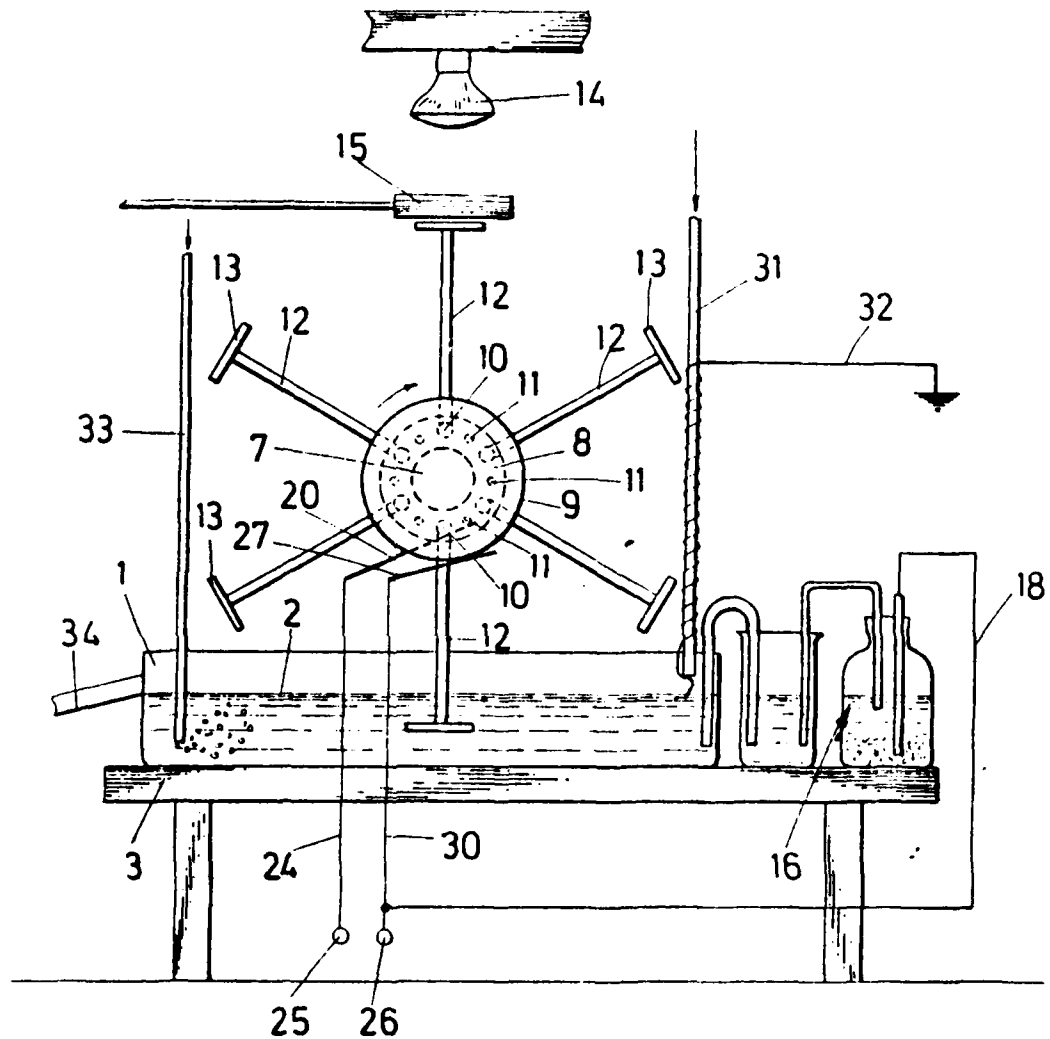
Figure 4 Semi logarithmic relationship between maximum pit depth and loss of weight for six aluminum alloys (industrial-marine atmosphere in Alicante) (from (3), p 307).



**Figure 5** Linear bilogarithmic relationship between maximum pit depth and weight loss for pure aluminum in different atmospheres (from (3), p 307)



**Figure 6** Linear bilogarithmic relationship between loss in tensile strength and exposure time for three aluminum alloys in an industrial atmosphere (from (3), p 309).



**Figure 7** A unit of the accelerated test method for atmospheric corrosion (CEBELCOR)



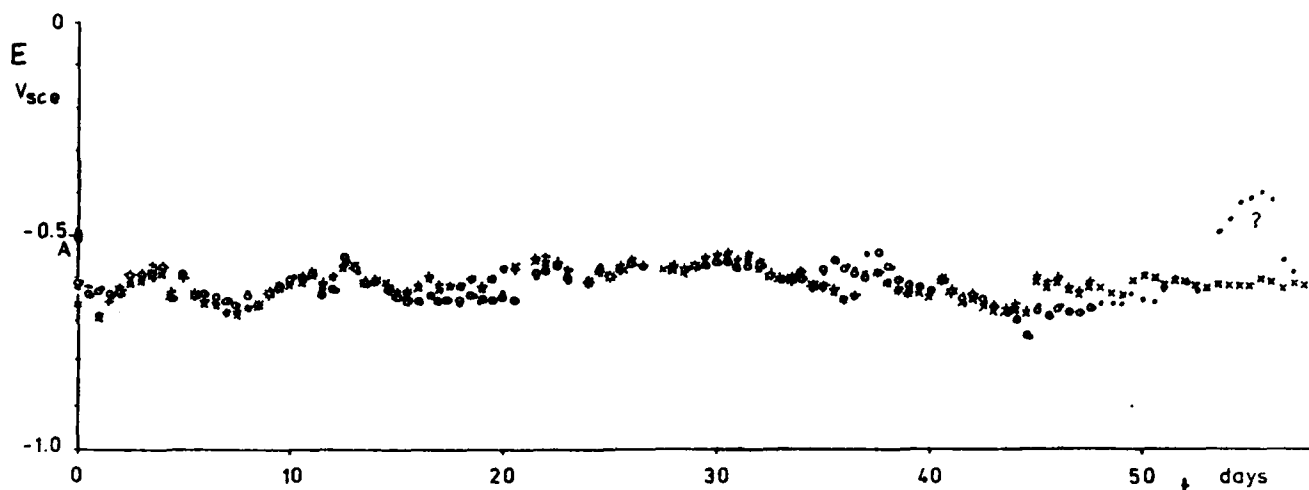


Figure 8 Electrode potential versus time for 3103-H24 (bare, etched) in  $\text{NaHSO}_3$   $10^{-4}$  M

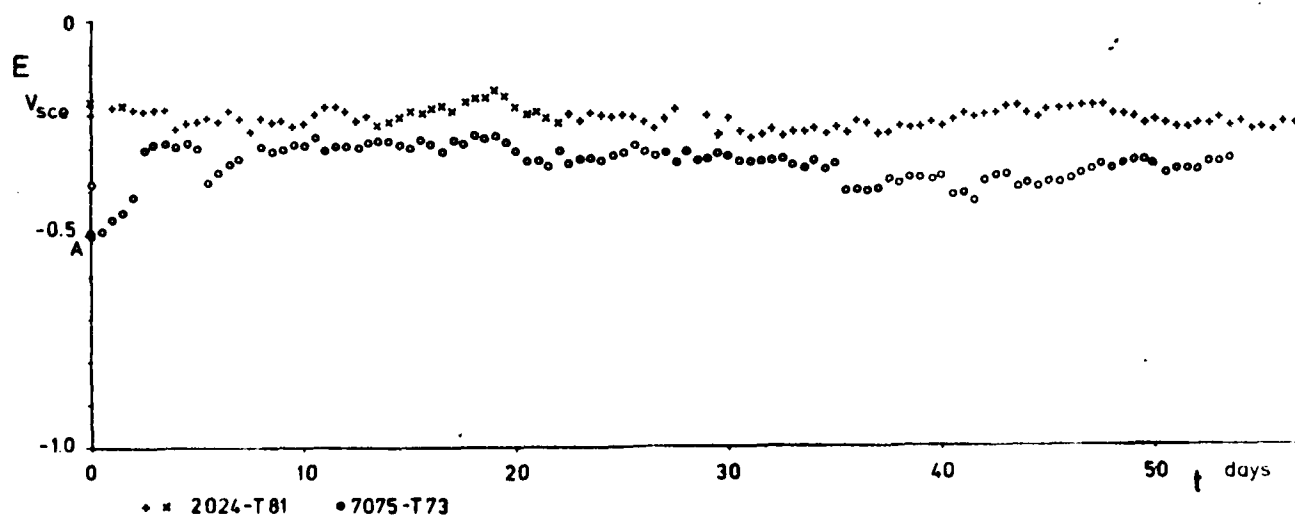


Figure 9 Electrode potential versus time for 2024-T81 and 7075-T73 (bare, etched) in  $\text{NaHSO}_3$   $10^{-4}$  M

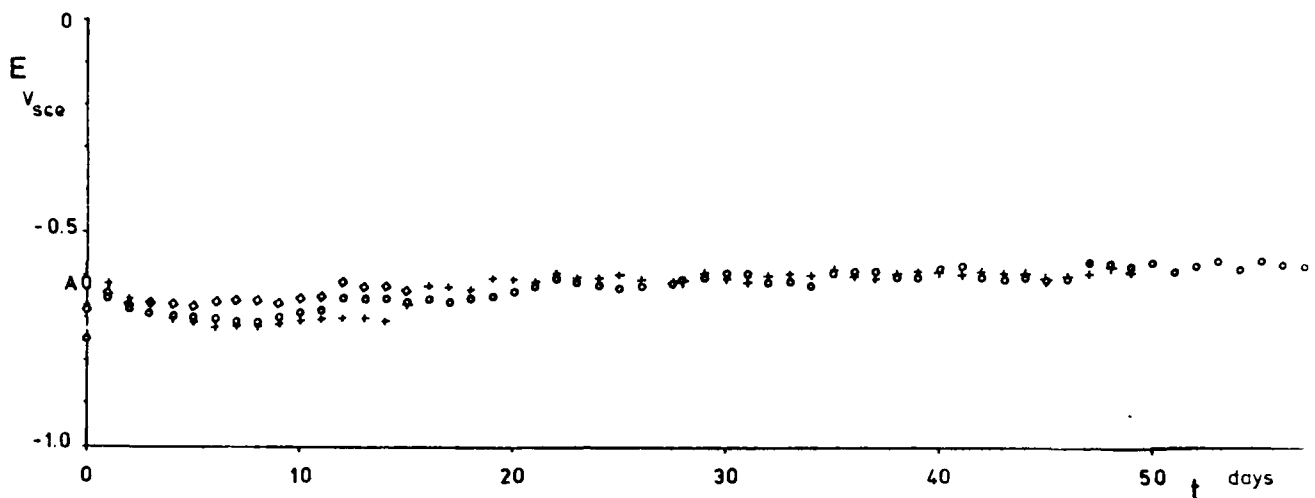


Figure 10 Electrode potential versus time for 3103-H24 (bare, etched) in 1 % sea water

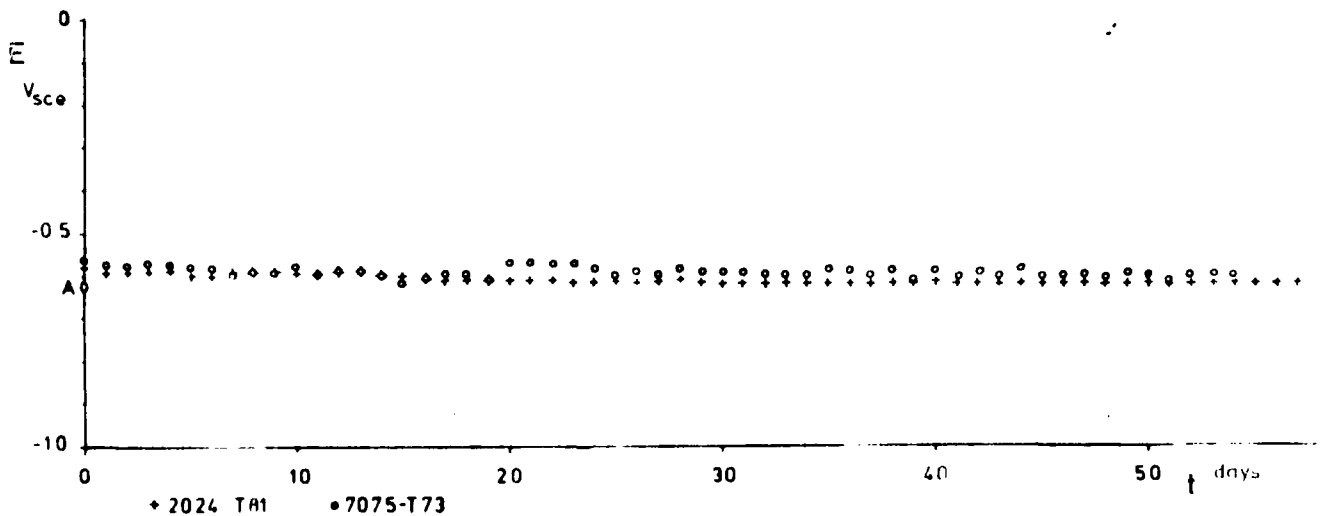


Figure 11 Electrode potential versus time for 2024-T81 and 7075-T73 (bare, etched) in 1 % sea water

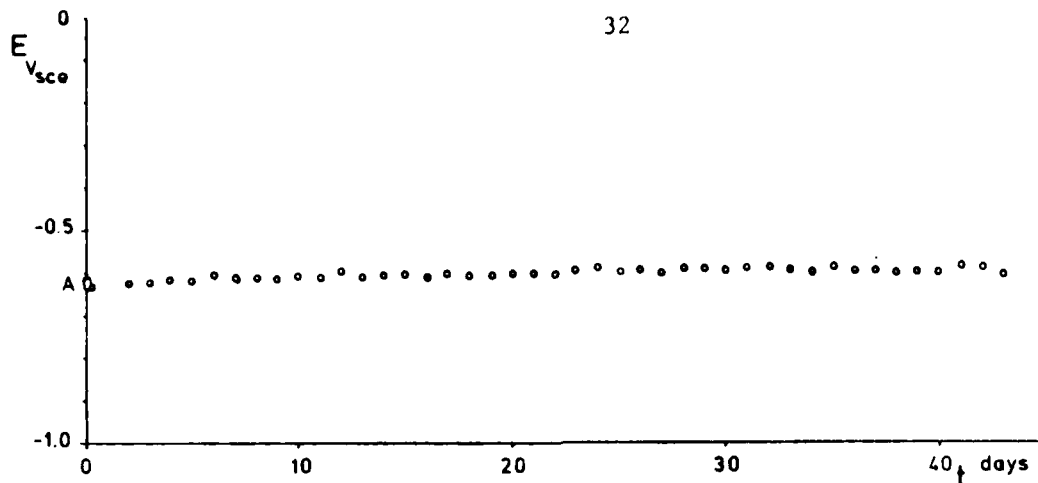


Figure 12 Electrode potential versus time for 3103-H24 (bare, as received)  
1 % sea water

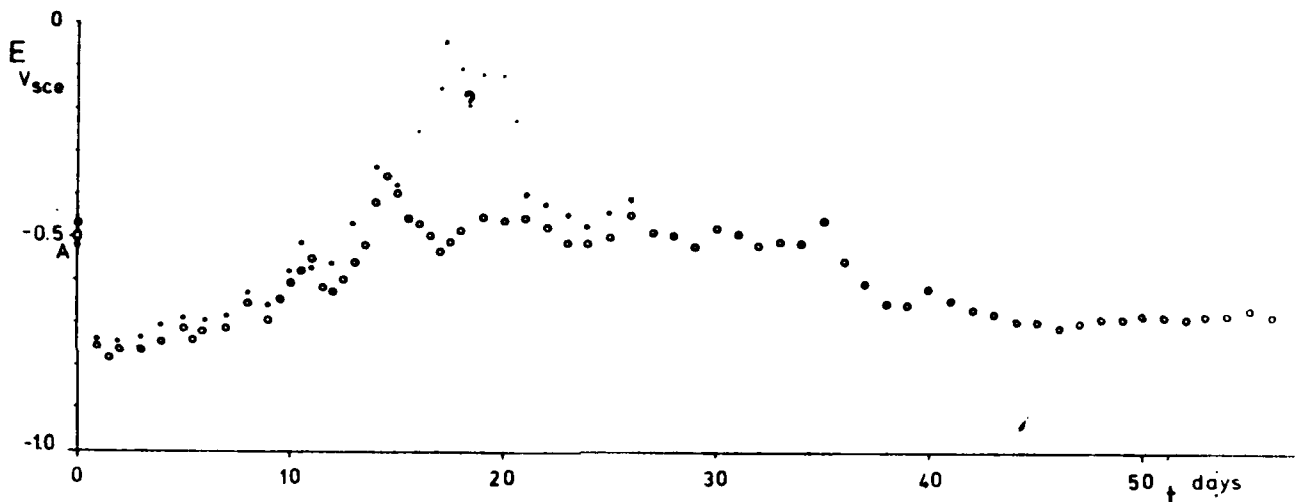


Figure 13 Electrode potential versus time for 7075-T73 (clad, etched) in  
 $\text{NaHSO}_3 \ 10^{-4} \text{ M}$

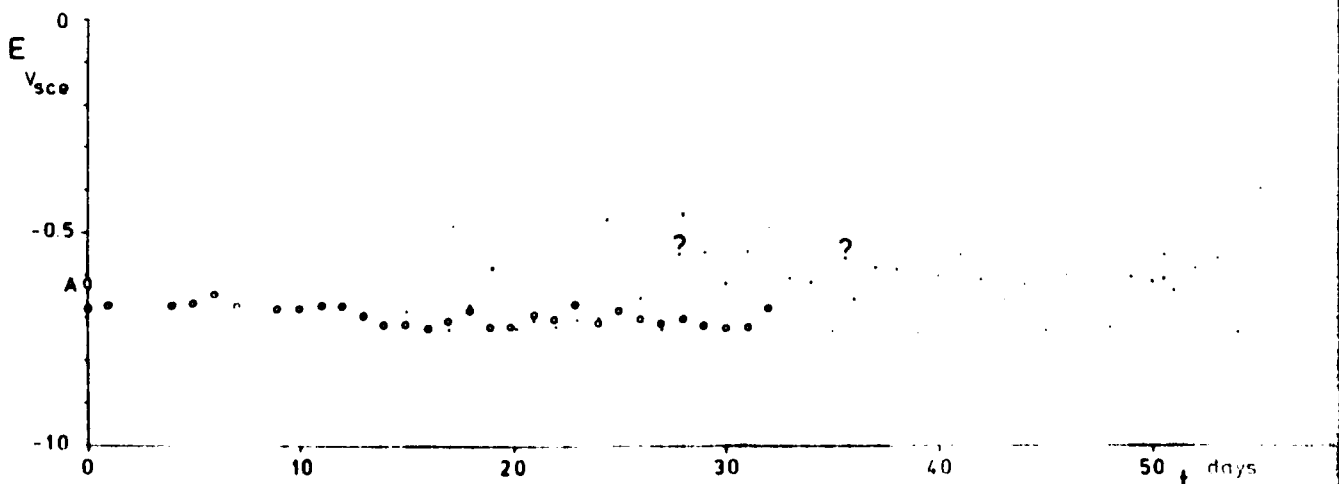
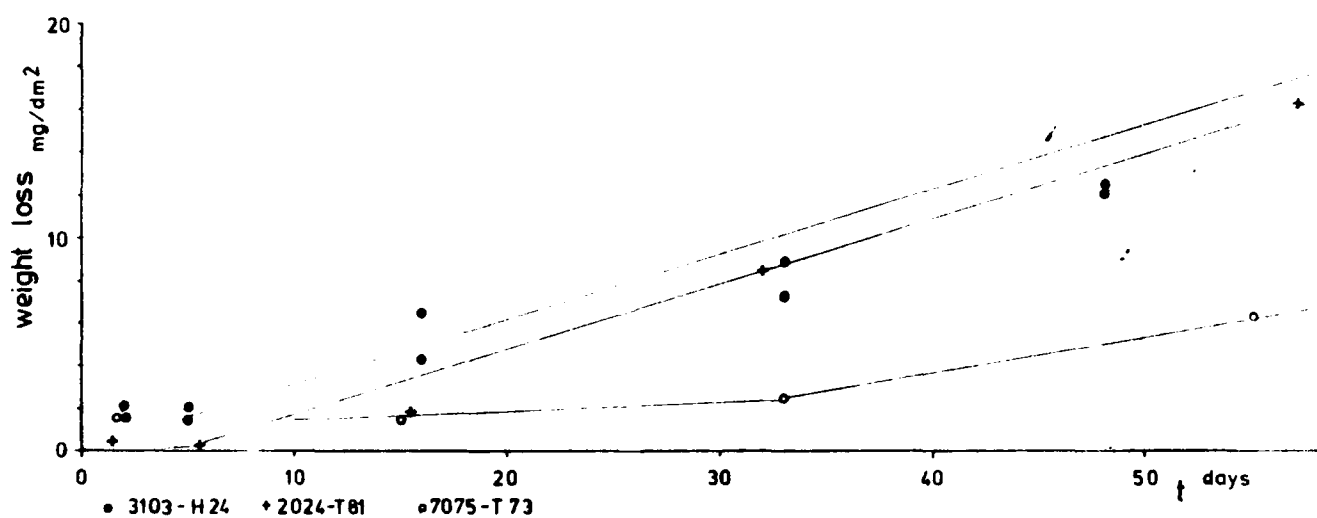
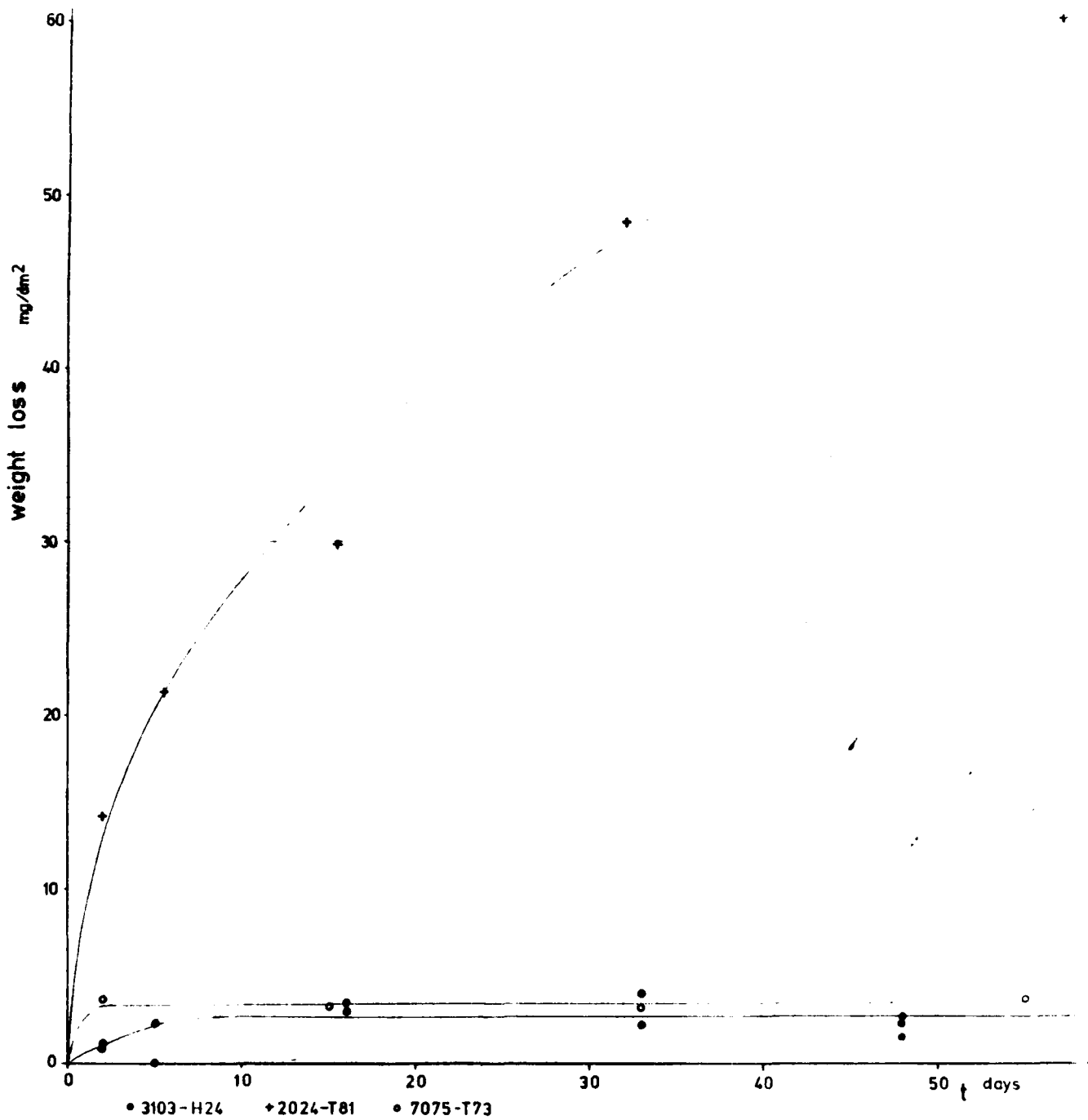


Figure 14 Electrode potential versus time for 7075-T73 (clad, etched) in  
1 % sea water



**Figure 15** Weight loss versus time for 3103-H24, 2024-T81 and 7075-T73  
(bare, etched) in  $\text{NaHSO}_3$   $10^{-4}$  M



**Figure 16** Weight loss versus time for 3103-H24, 2024-T81 and 7075-T73  
(bare, etched) in 1 % sea water

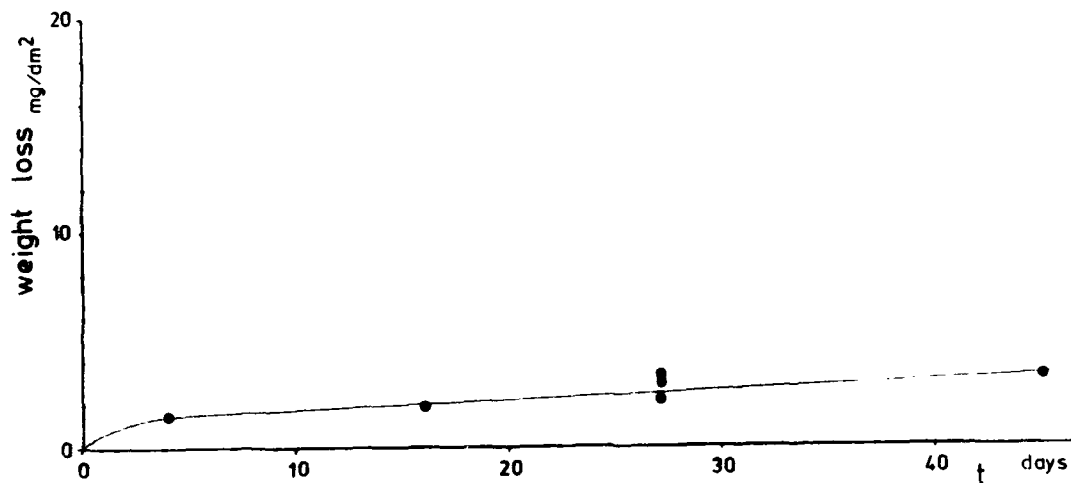


Figure 17 Weight loss versus time for 3103-H24 (bare, as received) in 1 % sea water

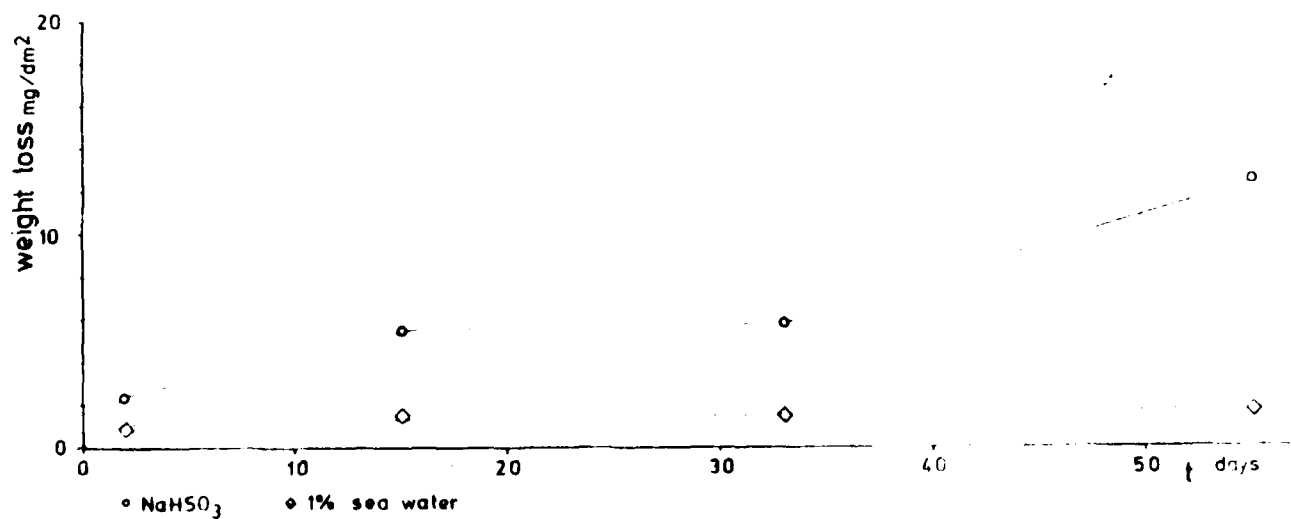


Figure 18 Weight loss versus time for 7075-T73 (clad, etched) in 1 % sea water

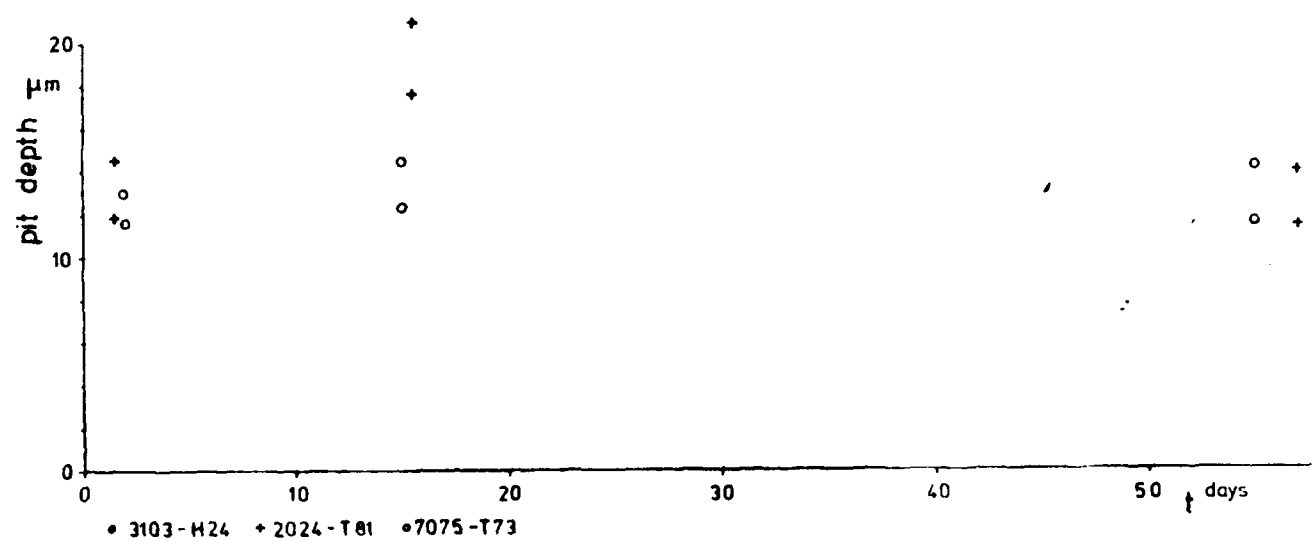
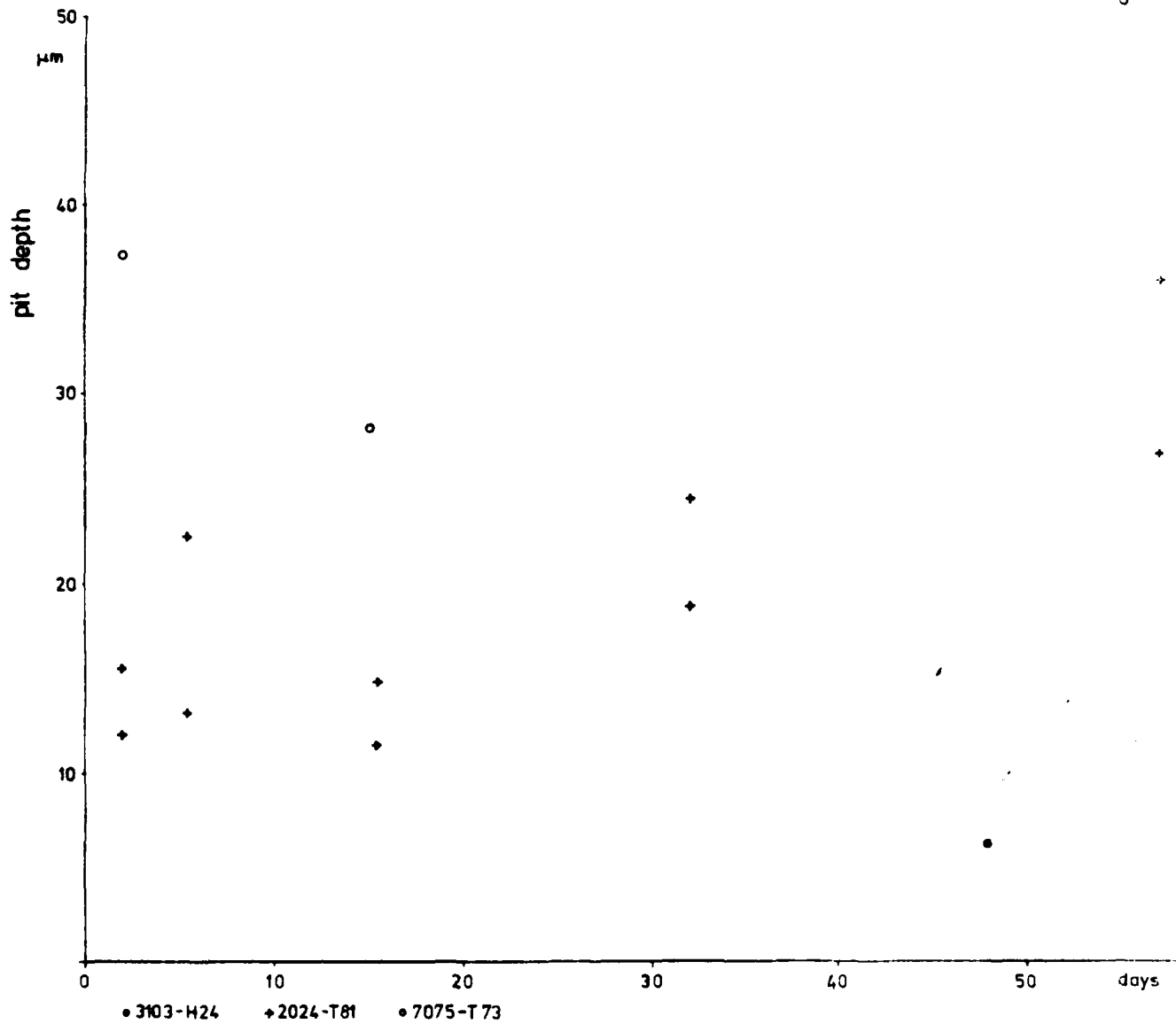
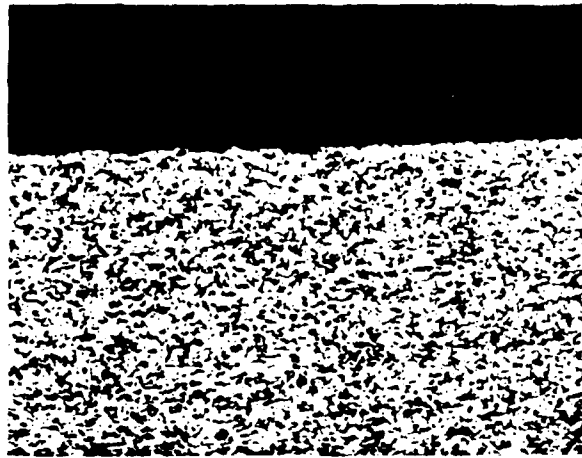


Figure 19 Pit depth versus time for 3103-H24, 2024-T81 and 7075-T73  
(bare, etched) in  $\text{NaHSO}_3$   $10^{-4}$  M



**Figure 20** Pit depth versus time for 3103-H24, 2024-T81 and 7075-T73  
(bare, etched) in 1 % sea water





a. 3103-H24



b. 2024-T81



c. 7075-T73

100  $\mu\text{m}$


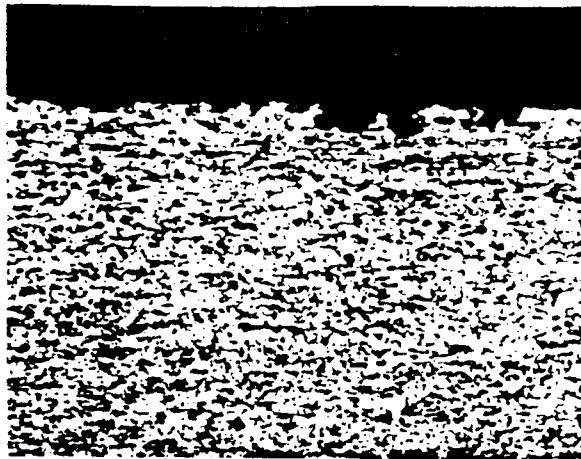
A horizontal line segment representing a scale of 100 micrometers.

Figure 21 Micrographs of 3103-H24, 2024-T81 and 7075-T73 tested 60 days in  $\text{NaOH}$ ,  $10^{-4}$  M (bare, etched)



a. 3103-H24



b. 2024-T81



c. 7075-T73

100  $\mu$ m

Figure 22 Micrographs of 3103-H24, 2024-T81 and 7075-T73 tested 60 days in 1% sea water (bare, etched)

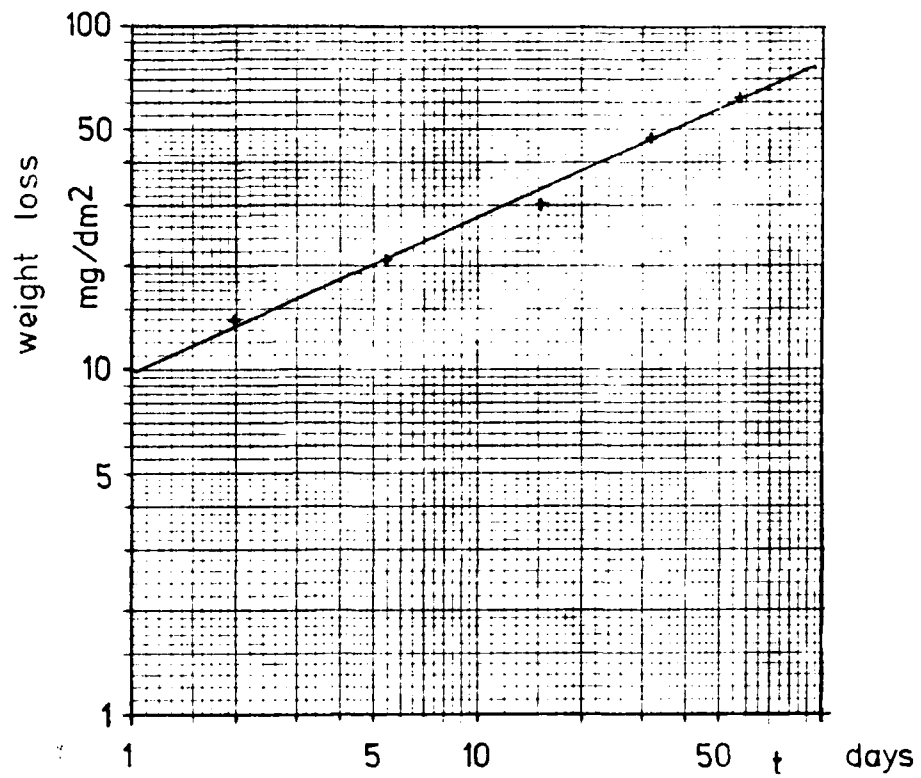


Figure 23 Log weight loss versus log time for 2024-T81 in 1% sea water (accelerated test)

**END**

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